NATIONAL BUREAU OF STANDARDS REPORT

7012

THERMAL AND SELF IGNITION PROPERTIES OF AMMONIUM PERCHLORATE AND PETN EXPLOSIVE

by

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U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

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U. S. Department of the Navy
Naval Ordnance Laboratory
White Oak, Maryland
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ABSTRACT

Measurements have been made of the specific heat, thermal conductivity and kinetic properties of pressed ammonium perchlorate and PETN explosive. Based upon these measurements estimates are provided on the self ignition hazard associated with use and bulk storage of such materials.

INTRODUCTION

At the request of the Naval Ordnance Laboratory determination of the thermal and kinetic properties of pressed ammonium perchlorate and PETN explosive was initiated. This report summarizes the results of such measurements and supplements results on three solid propellants (1) and six explosive materials (2) previously reported.

From these measurements and an analysis of the self heating reaction, an estimation may be made of the self ignition hazard associated with the use and bulk storage of such explosives. These measurements may also be useful for possible intercorrelation with an interpretation of sensitivity data.

MATERIALS

The explosives were furnished by the Naval Ordnance Laboratory in the shapes required for test. They consisted of pure pressed ammonium perchlorate and two PETN samples, one made up of 85% PETN and 15% wax and the other of 75% PETN and 25% wax.

A. Kinetic Measurements

The apparatus and method used for the self-heating studies and analysis of the data obtained have been described previously [1, 3]. Briefly, thermocouples were placed within a cylindrical specimen, 2 in. in diameter by 2 in. long, which was prepared by placing together 2 precut wafers 2 in. in diameter by 1 in. thick. The specimen was then placed in a stainless steel beaker and mounted within the furnace designed for the self-heating measurements. At least two tests for each explosive were performed in order to establish satisfactory reproducibility between duplicate tests. The slope of the time-temperature curve at several temperatures was plotted against reciprocal absolute temperature and the results are shown in Figure 1. A straight line has been drawn through one set of points in each case and the activation energy E determined from the slope. Comparative rates of self-heating at any temperature may be read directly from the graph. For example, at 160°C ($\frac{1}{T}$=0.002309) the pressed explosive PETN exhibited self-heating at a rate of 7.1 deg C/min, whereas any self-heating of ammonium perchlorate at this temperature was below the limit of sensitivity of the apparatus used.

The values of the kinetic constants determined from the lines in Figure 1 are listed in Table 1 for the applicable temperature ranges. Test observations and remarks are summarized below:

Self-heating tests on 75% PETN - 25% wax and 85% PETN - 15% wax indicated an apparent melting of the wax additive over the temperature range of 77 - 82°C. The samples exhibited negligible self-heating at temperatures below 135°C. However, upon reaching 135°C a very rapid combustion took place and the specimens were destroyed within 15 minutes.

Three tests were run on pressed ammonium perchlorate. From an initial furnace temperature of 190°C the material self-heated in 2 1/4 hours to 240°C, at which temperature an induction period of about 5 minutes' duration occurred. This effect was probably caused by a change in crystal structure of the material. After this short pause at 240°C, the ammonium perchlorate underwent a rapid combustion and the specimens were destroyed.

B. Specific Heat Measurements

For the specific heat measurements, Varsol was used as the heat transfer fluid because of its low heat capacity of 0.4370 cal/gm deg C, as measured over the experimental temperature range. Specimens for these measurements consisted of two pieces of explosive, each 1 7/8 by 2 by 1/2 in., and each piece was sealed for protection against possible attack by the Varsol by means of cellophane tape. The calorimeter was so constructed that the two pieces constituting a specimen formed two sides of a channel through which the Varsol was circulated by a centrifugal pump. The specific heat of each specimen was measured by substituting it for 63.4 g of the initial 175.4 g of Varsol in the half-pint Dewar flask calorimeter, and measuring the energy equivalent of the calorimeter and contents electrically. Storage batteries supplied electrical energy to a submerged cartridge heater, measurements being made of the heater current I, the heater resistance R, and the time of power input t. The energy input was calculated by the equation

$$E = \frac{I^2 Rt}{4.184} \text{ calories.}$$

From the value obtained for the calorimeter and 175.4 g of Varsol, and the values obtained when the specimens were tested, the specific heat of each specimen, including the cellophane wrapping, was obtained. The specific heat of the specimen alone was determined using a value of 0.32 cal/gm deg C for the specific heat of the cellophane. Three tests on each specimen were performed and inspection of the material after test showed no evidence of any Varsol leakage into the cellophane-packaged explosives. Results are summarized in Table 2.

C. Thermal Conductivity Measurements

Specimens for these measurements consisted of circular discs of 6-in. diameter and a uniform thickness of approximately 0.5 in.

The thermal conductivity was determined in the conductive disc apparatus (4) which consists of a stainless steel disc of 6-in. diameter sandwiched between two specimens, which in turn are sandwiched between two water-cooled brass plates. The central conductive disc is uniformly heated at the edge by means of electrical resistance wire set in an edge

groove. The heat generated at the disc edge tends to flow in the disc radially toward its center, and also from the disc through the two specimens to the two cold plates. These plates are maintained at a uniform temperature by circulating cold water through copper tubing soldered to them. Under steady state conditions, the temperature of the conductive disc decreases toward the center. By measuring the temperature of the conductive disc at the center and at a suitable radius (temperatures t_o and t respectively) the effective conductance of the specimens can be calculated if the temperature of the cold plates (t_c) and the conductivity and thickness of the disc metal are known.

It was decided to use only one explosive specimen for these measurements and therefore a dummy specimen was used in place of a duplicate. This dummy consisted of a 1 in. thick semi-rigid glass-fiber insulating board of stable, low thermal conductivity (0.348 mw/cm°C at 50°C). A thickness of 0.991 in. was maintained during use by three small fiber pegs thrust perpendicularly through the board. The lower cold plate of the apparatus, the dummy specimen, and the conductive disc were fastened together with rubber cement to form a sub-assembly.

During previous use, the apparatus had been calibrated by measurements on six specimens for which thermal conductances in the range 0.3 to 4.4 mw/cm^2°C were known from determinations made with the guarded hot plate apparatus (ASTM C177-45). A faired curve drawn through the six points obtained by plotting the known conductance against the measured ratio $\frac{t - t_c}{t_o - t_c}$ (designated $\frac{V}{V_o}$) for each material, provided a calibration curve for the apparatus. Departure of the individual points from the faired curve did not exceed one percent. Before making measurements on the PETN and ammonium perchlorate, a check measurement was made on one of the six calibration specimens (1.25 cm thick neoprene rubber) and the value obtained agreed with the previous measurement within two percent.

The specimen conductances were corrected to compensate for the change in the conductive disc conductivity when its mean temperature departed from the calibration temperature. Duplicate tests were run on each of the materials and results are summarized in Table 3.

D. Calculation of Critical Size

In order to estimate the critical size for ignition of a mass of self-heating material, the analysis presented by Enig, Shanks and Southworth [5] was used. This related the half-thickness of a material

of given thermal and kinetic properties with the temperatures at the center and the surface, under critical steady state conditions. The assumption was made that the kinetic properties measured over higher temperature ranges may be applied to the temperature range of practical interest for ordinary storage (20 - 100°C). It was further assumed that the measured thermal properties may be applied over the whole temperature range. These are broad assumptions, particularly for PETN for which the kinetic measurements were made on the liquid phase. Critical radius determinations for a sphere have been made for each explosive and are listed in Table 4 and shown graphically in Figure 2. It may be noted from the tables in Reference 4 that for a given surface temperature, the critical radius for a cylinder and the critical half-thickness for a semi-infinite slab are given very closely by 0.775 B_c and 0.514 B_c, respectively, where B_c is the critical radius for the sphere.

SUMMARY

Measurements of the specific heat, thermal conductivity and kinetic properties of pressed ammonium perchlorate and PETN explosive have been made and are listed in Tables 1 to 3. In the self-heating experiments on the PETN specimens an apparent melting of the wax additive occurred over the temperature range 77 - 82°C. The material exhibited negligible self-heating at temperatures below 135°C. However, upon reaching 135°C, a rapid combustion began and the specimens were destroyed within 15 minutes. Activation energy values, as measured by this method, were 32.2 $\frac{\text{k cal}}{\text{mole}}$ for the 85%PETN - 15% wax specimens. Comparison of the data shows close agreement between duplicate tests on each material and appears to indicate that the different amounts of wax additive present in the specimens tested had a negligible effect on the self-heating process of the PETN explosive material.

The activation energy of pressed ammonium perchlorate, as measured by this method was 29.7 k cal/mole over the temperature range of 205°C to 230°C. It appears, however, that the activation energy may be quite dependent upon physical structure as well as temperature. Although an accurate value could not be estimated, the activation energy for the pressed ammonium perchlorate above the temperature of crystal transformation (240°C) appeared to be somewhat greater than 40 k cal/mole.

ERRATA

Sentence in first paragraph of Summary beginning "Activation energy..." should read as follows: "Activation energy values, as measured by this method, were 32.2 $\frac{\text{k cal}}{\text{mole}}$ for the 75% PETN - 25% wax specimen and 33.8 $\frac{\text{k cal}}{\text{mole}}$ for the 85% PETN - 15% wax specimens."

The energy of activation for pure granular ammonium perchlorate of 0.91 gm/cm^3 density had previously been determined in the same apparatus, and mean values for the temperature range 205° to 270°C of E = 41.2 k cal/mole and A = 1.22 x 10^{16} $cal/sec\ cm^3$ were obtained (6). The present data on pressed ammonium perchlorate suggested the possibility that, in the earlier results on the granular perchlorate, some indication of a change in activation energy at the temperature of crystal transformation might have escaped notice and been obscured in the mean values reported. Re-examination of the earlier results, however, confirm the belief that the activation energy of the pure ammonium perchlorate in granular form did not undergo a significant change at 240°C.

A comparison of critical radius determinations under the given assumption is presented in Table 4 and Figure 2. Size limitations on the storage of bulk quantities of PETN and ammonium perchlorate, and careful control of temperature and ventilation conditions, seem justified on the basis of these calculations. Consideration must be given to melting or other phase transformations occurring at relatively low temperatures, for example, the melting of the wax additive in the PETN explosive specimens at 77° - 82°C.

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4. Robinson, H. E., Flynn, D. R. and Watson, T. W. "Measurements of the Thermal Conductivity of Several Explosives by the Conductive Disc Method," NBS Rept. 6527.

5. Enig, J. W., Shanks, D. and Southworth, R. W. "The Numerical Solution of the Heat Conduction Equation Occurring in the Theory of Thermal Explosions," NAVORD Rept. 4377 (1956). ASTIA Document No. AD-116 873.

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TABLE 1. KINETIC MEASUREMENTS

Material	Temperature Range	State	Activation Energy, E	Heat Generation Coefficient, A
	°C		k cal/mole	cal/sec cm^3
75% PETN - 25% Wax	135 - 175	Liquid	32.2	3.18×10^{15}
85% PETN - 15% Wax	135 - 175	Liquid	33.8	6.78×10^{15}
Ammonium Perchlorate NH_4ClO_4	205 - 230	Solid	29.7	4.83×10^{11}

TABLE 2. SPECIFIC HEAT MEASUREMENTS

Material	Sample Weight	Cellophane Weight	Temp. Rise	Energy Input, $\frac{I^2Rt}{4.184}$	Specific Heat	
					individual	mean
	g		deg C	Cal	cal/g °C	cal/g °C
75% PETN - 25% Wax	90.0339	5.3571	3.524	367.92	0.3414	
			3.472	363.66	0.3419	
			3.624	375.19	0.3375	0.340
85% PETN - 15% Wax	92.9239	4.8527	3.526	366.52	0.3277	
			3.507	367.71	0.3363	
			3.523	367.86	0.3326	0.332
Ammonium Perchlorate NH_4Cl_4	124.8187	4.0813	3.400	369.65	0.2785	
			3.362	370.35	0.2883	
			3.584	392.31	0.2926	0.286

TABLE 3. THERMAL CONDUCTIVITY MEASUREMENTS

Material	Density	Thickness	V/Vo	Cold Plate Temp.	Disc Temperature At R= 5.08 cm			Specimen Mean Temp.	Thermal Conductivity, k		
					Center		Mean		individual		mean
	gm/cm	cm		°C	°C	°C	°C	°C	mw/ cm°C	cal/ sec cm°C	cal/ sec cm°C
75% PETN-		1.270	1.1351	25.94	51.98	55.50	55	40	2.58	.000616	
25% Wax	1.452	1.270	1.1327	21.12	48.63	52.28	51	36	2.52	.000602	.000609
85% PETN-		1.270	1.1251	21.72	50.89	54.54	54	38	2.38	.000568	
15% Wax	1.524	1.270	1.1248	25.64	52.90	56.30	55	40	2.38	.000568	.000568
π Ammonium Perchlorate		1.270	1.2037	26.88	52.12	57.26	56	41	4.01	.000958	
NH_4ClO_4	1.834	1.270	1.2059	26.27	51.59	56.80	55	41	4.05	.000968	.000963

TABLE 4. CRITICAL SIZE CALCULATIONS

Material	Critical Radius of a Sphere at Surface Temperatures of 20°C (68°F) cm	ft	49.9°C (120°F) cm	ft	82.2°C (180°F) cm	ft	100°C (212°F) cm	ft
75% PETN - 25% Wax	2015	66	184	6.0	19.3	0.6	6.8	0.2
85% PETN - 15% Wax	4708	154	368	12	35.6	1.2	11.9	0.4
Ammonium Perchlorate NH_4ClO_4	23760	780	2646	87	321	10	128	4

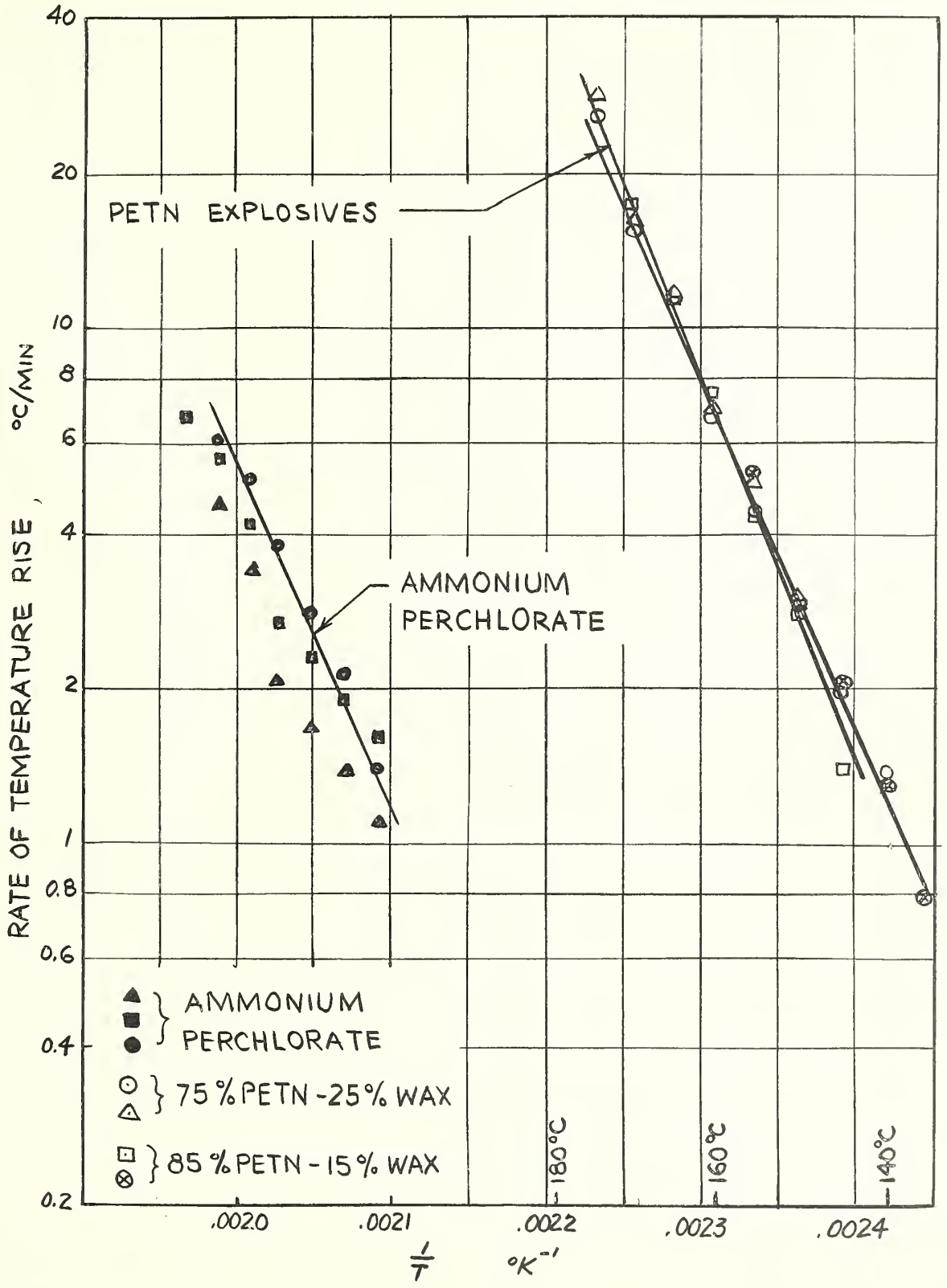

FIG. 1 ADIABATIC SELF-HEATING DATA FOR AMMONIUM PERCHLORATE AND PETN EXPLOSIVES

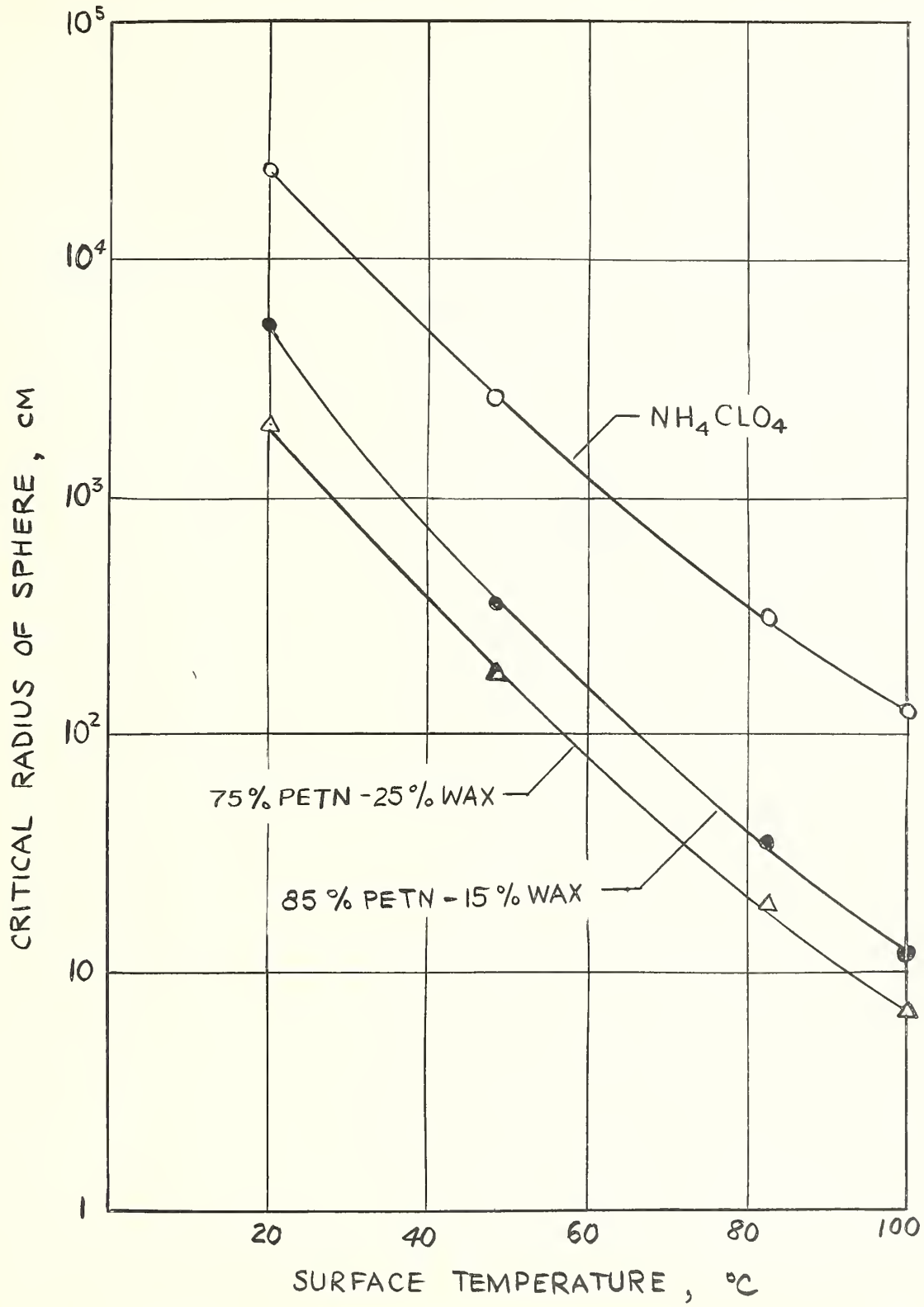

FIG. 2 COMPUTED CRITICAL RADII AND CRITICAL SURFACE TEMPERATURES FOR SPHERICAL PILES OF NH_4CLO_4 AND PETN EXPLOSIVES

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